J. Phys. Chem. A **1997,** *101,* 9405−9409

Accurate Calculations of the Electron Affinity and Ionization Potential of the Methyl Radical

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Received: March 18, 1997[⊗]

The electron affinity and ionization potential for the CH_3 radical have been calculated at high levels of *ab initio* molecular orbital theory. The best values are obtained by extrapolating CCSD(T)/aug-cc-pVxZ values where x = D, T, Q to the complete basis set limit. Zero-point energies were calculated at the CCSD(T)/aug-cc-pVTZ level and scaled to appropriate experimental values. The calculated values are EA(CH_3) = 1.64 ± 0.3 kcal/mol as compared to the experimental value of 1.84 ± 0.69 kcal/mol and IP(CH_3) = 9.837 ± 0.01 eV as compared to the experimental value of 9.843 ± 0.001 eV. The theoretical values included estimates of relativistic and core/valence correlation effects.

Introduction

Computational chemistry has made enormous strides over the past two decades due to continuing advances in hardware, software, and theoretical methods development. As a consequence, for chemical systems with fewer than ∼150 atoms, it is now a full-fledged partner with experimental methods, as judged by the large number of theoretical results that appear in the chemical literature. Thermodynamics, especially the area of thermochemistry, is one in which computational chemistry is playing an ever-increasing role. As experimental thermodynamic measurements become more difficult due to (1) the growing size of molecules of interest and (2) the demand for improved accuracy arising from needs such as chemical process modeling, computational methods become increasingly important. They are especially useful because of their potential for predicting the thermochemical properties of species that are kinetically unstable, e.g. radicals, anions, and cations. In this regard, it is essential to know *a priori* the accuracy and reliability that can be expected from a given method. In the absence of meaningful, rigorous error bars that can be assigned to a computational method, the best alternative is a sufficiently extensive set of benchmarks so that accuracies can be estimated from performance on “similar” chemical systems. We are especially interested in computational methods that do not involve the use of empirical parameters.

An area of obvious importance to many chemical processes, including combustion chemistry, is that of hydrocarbon radicals. One of the simplest is the methyl radical, CH_3. The heat of formation has been well established experimentally, as well as its ionization potential and electron affinity. The adiabatic ionization potential (IP) has been measured to be 9.843 ± 0.001 eV from spectroscopic studies.[1,2] There have been a number of photoionization studies which are in agreement with this value.[2] The literature contains a single photodetachment measurement of the adiabatic electron affinity (EA) of CH_3.[3] The reported value is very small, 0.08 ± 0.03 eV (1.84 ± 0.69 kcal/mol). Combined, these results provide reliable experimental values against which one can benchmark theoretical methods. Furthermore, there exist good spectroscopic studies of the radical[4,5] and there are some spectroscopic studies of the cation[5,6] which allow us to improve our estimates of zero-point vibrational energy corrections.

Experience with other small molecules suggests that extended basis set, highly correlated methods should be capable of accurately predicting the ionization potential of CH_3. The diffuse nature of the anion’s electron density translates into a requirement for extra diffuse basis functions if comparable accuracy in the electron affinity is to be achieved. The small size of the CH_3 electron affinity may indicate a need for special computational requirements. For example, one of the earlier attempts[7] to accurately calculate this value employed a polarized Slater basis set of the form (5s3p1d/2s1p) for CH_3 and a (5s5p1d/2s1p) set for CH_3^-. At the single and double excitation configuration interaction (CISD) level the actual calculated value was −8.3 kcal/mol for the adiabatic EA uncorrected for zero-point effects. The authors then estimated the electron affinity to be −2.7 kcal/mol if all effects were taken into account.

More recently, G1[8] and G2[9] estimates of the EA (0.01 and 0.04 eV, respectively, including zero-point effects) have been reported, both falling short of the experimental value of 0.08 eV. The zero-point energy correction for these methods is 0.71 kcal/mol (0.03 eV), favoring CH_3^-. Thus, at the G1 level, CH_3^- is electronically unbound, while at the G2 level it is bound by 0.01 eV. However, both the G1 and G2 estimates include correction factors based on the number of electron pairs. These correction factors are taken from errors in the calculation of the H atom and H_2 molecular energies. The magnitude of the corrections are nontrivial, amounting to 3.73 kcal/mol (0.16 eV) for G1 and 3.14 kcal/mol (0.14 eV) for G2. The electronic value of EA(CH_3) at the G1 level, without correction factors, is −4.2 kcal/mol and at the G2 level is −2.9 kcal/mol. Thus, all of the apparent G1 and G2 electronic binding energy for CH_3^- arises from the correction factors.

In the present work, we report a set of high-level *ab inito* calculations of EA(CH_3) and IP(CH_3) at the coupled cluster level of theory in an effort to improve the accuracy with which we know these properties.

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

S1089-5639(97)00964-X CCC: $14.00

TABLE 1: Optimized CCSD(T) Geometries (in Å and deg)

	CH_3^-			CH_3	CH_3^+
method/basis	*R*(CH)	*A*(HCH)	*D*(HHCH)	*R*(CH)	*R*(CH)
MP2/aug-TZ2PF	1.097	110.1		1.074	1.085
CCSD(T)/aug-cc-pVDZ	1.1209	107.8	116.0	1.0932	1.1035
CCSD(T)/aug-cc-pVTZ	1.1047	108.7	118.2	1.0795	1.0907
CCSD(T)/aug-cc-pVQZ	1.1021	109.1	119.4	1.0780	1.0893
est CBS limit[a]	1.101	109.4	120.8	1.077	1.089
expt				1.079	(1.087)

[a] Based on a three-parameter exponential fit of the form $F(x) = A_{CBS} + B\exp(-Cx)$, $x = 2, 3, 4$ for DZ−QZ basis sets.

TABLE 2: Calculated Harmonic Vibrational Frequencies (in cm^{-1})

	CH_3^-			
method/basis	a_1	e	a_1	e
CCSD(T)/aug-cc-pVDZ	809.3	1396.9	2853.7	2947.3
CCSD(T)/aug-cc-pVTZ	783.8	1420.8	2890.6	2980.9
MP2/aug-TZ2PF	753.6	1426.2	2978.7	3091.5
scaled		1398	2788	2859
MP2/aug-TZ2PF (D_{3h})	627i	1376	3110	3265

	CH_3			
method/basis	a_2''	e′	a_1'	e′
CCSD(T)/aug-cc-pVDZ	498.1	1405.8	3101.7	3290.5
CCSD(T)/aug-cc-pVTZ	496.6	1418.9	3114.9	3295.1
MP2/aug-TZ2PF	456.4	1437.4	3180.5	3372.2
expt	606.5	1396	3004.4	3160.8

	CH_3^+			
method/basis	a_2''	e′	a_1'	e′
CCSD(T)/aug-cc-pVDZ	1417.2	1428.1	3036.0	3246.1
CCSD(T)/aug-cc-pVTZ	1422.0	1429.0	3039.7	3237.5
MP2/aug-TZ2PF	1445.1	1449.6	3098.8	3305.5
expt	1380		(3023)	3108.4
scaled	1380	1406	2932	3108.4

TABLE 3: Zero-Point Energies (kcal/mol)

method/basis	CH_3^-	CH_3	CH_3^+
CCSD(T)/aug-cc-pVDZ	17.66	18.57	19.72
CCSD(T)/aug-cc-pVTZ	17.84	18.64	19.72
MP2/aug-TZ2PF	18.24	18.94	20.08
best estimate	17.07	18.11	19.06

Methods

The coupled cluster calculations included single and double excitations with a noniterative correction for triples (CCSD(T) for closed shell species, UCCSD(T) for open shell species in Gaussian94, and R-UCCSD(T) for open shell species in MOLPRO).[10] The one-particle basis sets were taken from the correlation-consistent basis set family.[11] Unless otherwise noted, the carbon inner shell pair was treated as a frozen core in all correlated calculations. Only the spherical components of the d, f, and g functions were used.

Calculations were done with the Gaussian-94,[12] MOLPRO-96,[13] and MELDF-X[14] programs on SGI Power Challenge workstations. The geometries and frequencies were initially optimized with a large polarized triple-ζ valence basis set augmented by diffuse functions[15,16] at the MP2 level.[17] This geometry was used for single-point CCSD(T) calculations[10] with the augmented correlation-consistent basis sets (aug-cc-pVxZ where x = D, T, Q corresponding to the double-, triple-, and quadruple-ζ levels).[11] Subsequently, we reoptimized the geometries with the aug-cc-pVDZ through aug-cc-pVQZ basis sets and calculated harmonic frequencies at the double- and triple-ζ levels by using numerical differencing techniques because analytical derivatives were not available. In order to estimate values at the complete basis set (CBS) limit, we used a three-parameter exponential fitting function[18] of the form

$$F(x) = A_{\mathrm{CBS}} + B\mathrm{e}^{-Cx} \tag{1}$$

where $x = 2$, 3, and 4 for DZ, TZ, and QZ basis sets.

Results

The CCSD(T) optimized geometries are shown in Table 1. Since CH_3 is planar (D_{3h}), there is only one optimizable geometry parameter. The calculated R_{CH} bond length of 1.077 Å at the CBS limit is in excellent agreement with the experimental value of 1.079 Å obtained from B_0 for CD_3.[1,4b] The MP2/aug-TZ2PF value is too short by 0.005 Å, whereas the CCSD(T) values for the triple- and quadruple-ζ basis sets are in much better agreement with experiment. The CCSD(T)/aug-cc-pVDZ value is too large by 0.014 Å. For CH_3^- the additional electron results in a pyramidal geometry (C_{3v}) with a bond angle near tetrahedral and bond lengths that are longer than the value in CH_3. The CCSD(T)/CBS bond angle is essentially tetrahedral and the extrapolated bond length is 0.024 Å longer than the extrapolated value for the neutral radical. The MP2/aug-TZ2PF value is 0.004 Å shorter than the CCSD(T)/CBS value, just as was found for the neutral where the difference is 0.003 Å. The CH_3^+ cation is also expected to be planar (D_{3h}). Calculations show that the bond distance is ∼0.01 Å longer than the CH bond length in the neutral, in good agreement with the estimated experimental value[6b] of 1.087 Å.

Calculated harmonic frequencies are listed in Table 2. All of the vibrational frequencies for the CH_3 radical have been measured experimentally. The calculated harmonic stretches at the CCSD(T)/aug-cc-pVTZ level are larger than the experimental anharmonic values by 4.2% for the e′ mode[4c] and 3.7% for the a_1' mode.[4a] The close agreement between the theoretical harmonic value and the experimental anharmonic value for the degenerate e′ bend suggests that there is little anharmonicity in this mode. The calculated value is only 1.6% larger than the experimental value. There is a significant difference between the calculated and experimental values for the inversion mode. However, previous studies[4b,7] have shown that this mode is quite anharmonic in the bottom part of the well with a negative anharmonicity. Thus, it is not surprising that the calculated frequency is lower than the experimental value by so much. Therefore, we have chosen to employ the calculated zero-point energy of 281 cm^{-1} previously reported by one of us[7] based on a solution of the one-dimensional Schrödinger equation for this mode. The calculated 0−1 transition at this level[7] is 612 cm^{-1}, compared to an experimental value of 606.5 cm^{-1}.[4b]

The stretching frequencies of the CH_3^- anion are predicted to be significantly smaller than the frequencies of the neutral radical, consistent with the longer C−H bond in the anion. We give scaled values in Table 2 for the stretches and the degenerate bend based on scaling factors from the CH_3 radical. The CH_3^- anion has a low inversion barrier which can affect the zero-point energy and the frequency of this mode. The inversion barrier has previously been calculated to be 1.95 kcal/mol at

TABLE 4: Total CCSD(T) Energies (hartrees)

basis	geometry	CH_3^- ($^1A_1$)[a]		CH_3 ($^2A_2''$)	CH_3^+ ($^1A_1'$)
aug-cc-pVDZ	MP2	−39.720 36	(−39.715 55)	−39.723 96	−39.370 37
aug-cc-pVTZ	MP2	−39.763 20	(−39.758 87)	−39.763 59	−39.405 66
aug-cc-pVQZ	MP2	−39.773 87	(−39.769 96)	−39.773 29	−39.414 45
est CBS limit[c]	MP2	−39.777 40		−39.776 44	
basis	geometry	CH_3^- ($^1A_1$)	CH_3 ($^2A_2''$)	CH_3^+ ($^1A_1'$)[b]	
aug-cc-pVDZ	CCSD(T)	−39.721 23	−39.724 71	−39.371 00	(−39.370 80)
aug-cc-pVTZ	CCSD(T)	−39.763 32	−39.763 66	−39.405 71	(−39.405 47)
aug-cc-pVQZ	CCSD(T)	−39.773 92	−39.773 34	−39.414 48	(−39.414 23)
est CBS limit[c]	CCSD(T)	−39.777 49	−39.776 54	−39.417 45	(−39.417 20)

[a] D_{3h} geometry for CH_3^- in parentheses. [b] Vertical ionization energy calculated at the neutral geometry in parentheses. [c] The estimated complete basis set limit was obtained from a three-parameter exponential fit with eq 1.

TABLE 5: CCSD(T) Electron Affinities and Ionization Potentials (kcal/mol)

basis	$EA_{e(adiabatic)}$		EA(adiabatic)
aug-cc-pVDZ	−2.19		−1.28
aug-cc-pVTZ	−0.22		0.58
aug-cc-pVQZ	0.36		1.16[d]
est CBS limit[a]	0.60[b] (0.60)[c]		1.64
basis	IP_e(adiabatic)	IP(adiabatic)	IP_e(vertical)
aug-cc-pVDZ	221.96	223.11	222.08
aug-cc-pVTZ	224.62	225.70	224.77
aug-cc-pVQZ	225.19	226.27[d]	225.34
est CBS limit[a]	225.33[b] (225.35)[e]	226.28	225.49

[a] The estimated complete basis set limit was obtain from a three-parameter exponential fit. [b] Obtained by extrapolating the individual energies. [c] Obtained by extrapolating the EAs. [d] Zero-point energy correction taken from the aug-cc-pVTZ result. [e] Obtained by extrapolating the IPs.

the CISD+Q level with the STO basis set described above.[7] The zero-point contribution for this mode was calculated to be 325 cm^{-1} with an inversion splitting of 27 cm^{-1}, based on the solution of the vibrational Schrödinger equation and the potential calculated previously.[7] We adopted this value for the zero-point contribution of this mode rather than our directly calculated value of 392 cm^{-1} at the CCSD(T)/aug-cc-pVTZ level. We recalculated the inversion barrier using an optimized MP2/TZVP geometry (r_{CH} = 1.082 Å). At the CCSD(T)/aug-cc-pVQZ level, the electronic energy barrier was 2.45 kcal/mol. The unscaled zero-point correction was 0.39 kcal/mol, using the above value of 325 cm^{-1} for the inversion mode of CH_3^-. Therefore, the final estimate of the inversion barrier was 2.06 kcal/mol. The zero-point energies are given in Table 3.

The degenerate stretching frequency for CH_3^+ has been measured experimentally as 3108.4 cm^{-1} and the symmetric stretch has been estimated to be 3023 cm^{-1}. The calculated value at the CCSD(T)/aug-cc-pVTZ level is 4.2% too high for the e′ mode. The symmetric stretch is only 0.6% too high, suggesting that the experimental estimate for the symmetric stretch is too high.[6b] We thus prefer to use the scaling factor from CH_3 for the symmetric stretch to estimate the zero-point energy. The inversion frequency is calculated to be 3.0% too high, compared to experiment.

Total energies are listed in Table 4 and the calculated electron affinities are in Table 5, where it can be seen that the added electron in CH_3^- is unbound at the CCSD(T)/aug-cc-pVDZ level of theory, even with zero-point corrections. It is also unbound electronically at the CCSD(T)/aug-cc-pVTZ level, but when zero-point corrections are included, the EA becomes slightly positive. The first time that the electron is bound electronically is at the CCSD(T)/aug-cc-pVQZ level (EA_e = 0.36 kcal/mol). Extrapolation by use of eq 1 of the electron affinities or the total energies to the complete basis set limit (see Figure 1) gives an electronic value of 0.60 kcal/mol, and inclusion of the zero-point effects gives 1.64 kcal/mol (0.07 eV), in excellent agreement with the experimental value[3] of 1.84 ± 0.69 kcal/mol (0.08 + 0.03 eV). It is interesting to note that 63% of the binding energy of the electron is due to zero-point effects. We estimate that deuteration, i.e. formation of CD_3^-, would lower the binding energy to 1.34 kcal/mol. This is consistent with the fact that the electron affinity of CD_3 was more difficult to measure. The largest error limits in our calculation are in the zero-point energies, notably for the anion. We estimate that the errors in these values are on the order of less than 0.2 kcal/mol. The error in the electronic value for EA is less than 0.1 kcal/mol, giving EA(CH_3) = 1.64 ± 0.3 kcal/mol.

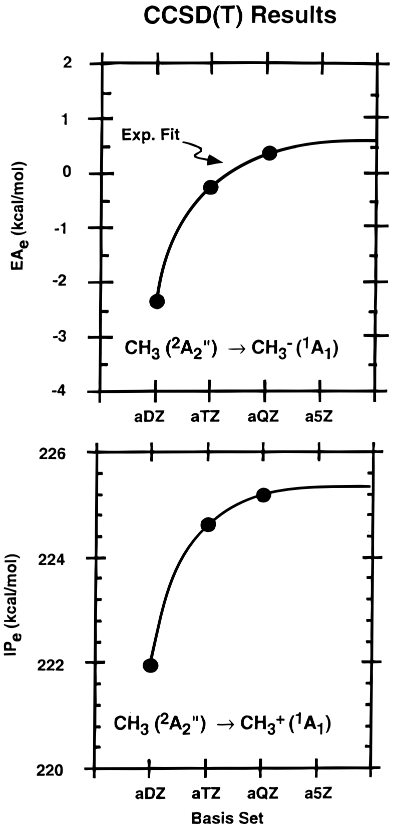

Figure 1. Basis set convergence of the electronic components of the adiabatic electron affinity and ionization potential using frozen core CCSD(T) energies.

The mass−velocity and one-electron Darwin relativistic corrections were evaluated for CH_3 and CH_3^- at their respective CCSD(T)/aug-cc-pVTZ geometries. For light elements, these are expected to be the dominant components of the Breit−Pauli Hamiltonian. First-order perturbation theory predicts a total differential effect on EA_e of less than 0.01 kcal/mol, which is

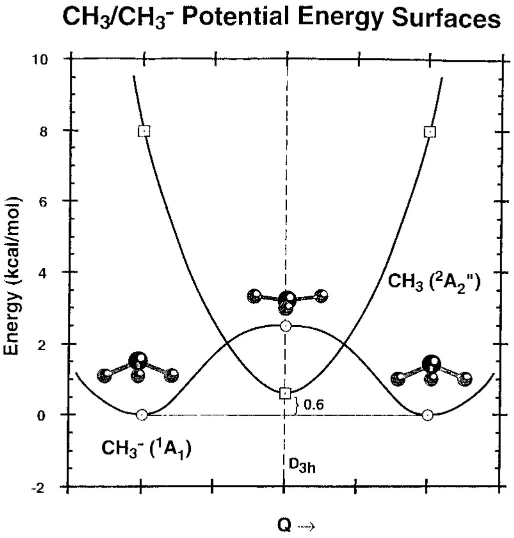

Figure 2. Schematic representation of the CH_3 and CH_3^- potential energy surfaces at the CCSD(T)/aug-cc-pVQZ level of theory. The neutral curve has been shifted upward 0.24 kcal/mol to coincide with our complete basis set estimate of the electron affinity.

below the uncertainty associated with this method for estimating the relativistic effects.

At the planar geometry, the electron is unbound even at the complete basis set limit. At the CCSD(T)/aug-cc-pVQZ level with the MP2 geometries, the planar anion is 2.12 kcal/mol above the energy of radical. At the CCSD(T)/aug-cc-pVQZ level with the CCSD(T)/aug-cc-pVQZ geometry for the radical, the anion is 2.15 kcal/mol above the radical (see Figure 2). The anion is created at a reasonably high temperature in the discharge and should exhibit significant populations in the inversion mode. As the molecule increases in energy in the inversion mode, the CH_3 and CH_3^- curves cross before the D_{3h} geometry is attained as shown in Figure 2 and the electron should autodetach. The fact that the anion is observed suggests that the electron does not regularly autodetach and that the motion in the inversion mode could be dominated by tunneling phenomena. We have also calculated the energy of the CH_3 radical at the optimum CH_3^- geometry. The radical is 7.4 kcal/mol above the lowest energy of the radical, and we can thus estimate that the vertical electronic detachment energy is 8.0 kcal/mol.

The ionization potential of CH_3 can also be calculated quite accurately. The electronic energy converges more rapidly for the ionization potential than for the electron affinity. The difference between the extrapolated value and the CCSD(T)/aug-cc-pVQZ is only 0.14 kcal/mol. Inclusion of the zero-point effect increases the IP by 0.95 kcal/mol to give a value of 226.28 kcal/mol (9.81 eV), in good agreement with the experimental value of 226.9 kcal/mol (9.84 eV). First-order perturbation theory predicts a relativistic correction of less than 0.06 kcal/mol (0.003 eV), lowering the ionization potential.

In order to estimate the effect of core−valence correlation, all-electron CCSD(T) calculations were performed on CH_3 and CH_3^+ at the optimized aug-cc-pVQZ CCSD(T) geometries with the cc-pwCVQZ basis set.[19] This basis set has the needed functions for core−valence effects and should be very nearly converged with respect to the basis set limit of the core−valence effect. At this level, the IP with only the valence electrons correlated is 224.91 kcal/mol, only 0.4 kcal/mol from the estimated complete basis set limit at 225.33 kcal/mol. With all electrons correlated, the IP is 225.39 kcal/mol, giving a core−valence correction of +0.48 kcal/mol. Adding this correction to the above value including the relativistic correction of 0.06 kcal/mol gives an IP of 226.82 kcal/mol (9.837 eV), within 0.14 kcal/mol (<0.01 eV) of the experimental value. On the basis of our calculated values, we estimate that there is an error limit of 0.2 kcal/mol (0.01 eV) in the zero-point energies and potentially another 0.1 kcal/mol in the valence electron energy difference, yielding a final calculated IP(CH_3) = 226.8 ± 0.3 kcal/mol (9.837 ± 0.01 eV). Given our error limits due to the zero-point effects, this provides excellent agreement with the experimental value. We also note that the vertical IP is only 0.16 kcal/mol (0.007 eV) larger than the adiabatic value.

Acknowledgment. This research was supported by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830 (Division of Chemical Sciences, Office of Basic Energy Sciences, and the Environmental Technology Partnerships Program). The Pacific Northwest National Laboratory is operated by Battelle Memorial Institute. We also wish to thank the Scientific Computing Staff, Office of Energy Research, U.S. Department of Energy, for a grant of computer time at the National Energy Research Scientific Computing Center (Berkeley, CA).

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